



## Catalytic Effects of Aluminum Butoxyethoxide in Sol-Gel Hybrid Hard Coatings

TAE-HO LEE, EUN-SEOK KANG AND BYEONG-SOO BAE

Laboratory of Optical Materials and Coating (LOMC), Department of Materials Science and Engineering,  
Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea

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**Abstract.** Hybrid inorganic-organic hard coatings on PMMA substrate were obtained by sol-gel reaction of 3-glycidoxypropyltrimethoxysilane(GPTS), tetramethyl orthosilicate(TMOS) and aluminum butoxyethoxide ( $\text{Al}(\text{OEtOBu})_3$ ). The catalytic effect of aluminum butoxyethoxide on inorganic condensation and epoxide polymerization has been studied by  $^{13}\text{C}$ ,  $^{29}\text{Si}$  nuclear magnetic resonance spectroscopy and by Fourier transformed infrared spectroscopy. Hardness of hybrid inorganic-organic materials were measured by nanoindenter and mainly influenced by the extent of epoxide polymerization and inorganic condensation of their coating catalyzed by aluminum butoxyethoxide.

**Keywords:** hard coating, sol-gel process, hybrid materials, catalyst, nanoindenter

### 1. Introduction

Many transparent polymer materials such as poly(methyl methacrylate) (PMMA), bisphenol-A polycarbonate(bis-A PC), diallyl diglycol carbonate (CR-39) have excellent optical transparency and their density are lower than that of the inorganic glasses and can be utilized as windows, lenses or other optical devices. However, because of their poor abrasion resistance, polymeric materials often lose transparency during daily use and maintenance. Thus, the hard coatings have been developed over the past few years by photopolymerization, thermal polymerization and silicone modification [1].

In last years, hybrid inorganic-organic materials have been researched as hard coatings for polymer materials [2–5]. Most of hard coatings were usually obtained by sol-gel process. Schmidt et al. [6–9] have developed hard coatings using metal or semi-metal oxide colloids such as alumina, zirconia, titania, or silica together with epoxy and methacrylate functionalized alkoxysilanes as major components. For epoxy functionalized alkoxysilane based hybrid ma-

terials, thermally and UV-curable coatings are available for scratch resistance, and the former types show higher abrasion resistance. Especially, Al-O containing epoxysilane-based hybrid coatings show the excellent abrasion resistance, and can be hardened at temperatures between 100–150°C which are suitable for polymer substrates with sufficient thermal stability [10–12].

3-Glycidoxypropyltrimethoxysilane (GPTS) has been widely used as a precursor in the synthesis of epoxysilane-based hybrid materials. Organic group of GPTS which contains an epoxide ring can be cross-linked to form a poly(ethylene oxide) chain and acts as network former. The density of hybrid materials with the polymerizable epoxide group of the GPTS is higher than that with the organically modified alkoxides whose organic groups are network modifiers [11]. The use of the GPTS is appropriate for thermal curable hard coating systems, due to their low curing temperatures required by the processing for polymer substrates. In order to obtain the excellent abrasion resistance in thermally curable GPTS-based hard coating system, the catalytic effects on epoxide polymerization and

inorganic condensation are necessarily required. It is well known that the epoxide ring opening reaction, which is necessary for the epoxide polymerization, can be catalyzed by amine, Ti, Zr, Al alkoxide and boron trifluoride diethyl etherate. Also, their alkoxides can be used for catalysts for inorganic condensation in sol-gel reaction [13–17]. In particular, the strong catalytic effects of Al-alkoxide and boron trifluoride diethyl etherate on both reactions have been already investigated [14, 16]. The catalytic reactions and structures of the GPTS-based hybrid materials were the subject of several specific studies [17–20].

The present work is to investigate the relationship between structure and mechanical properties (hardness) of the GPTS-based hybrid hard coatings depending on degree of polymerization and condensation catalyzed by the aluminum alkoxide concentration.

## 2. Experiments

### 2.1. Preparation of Coating Solution

GPTS and tetramethoxyorthosilicate (TMOS) used as the precursors. Boron trifluoride diethyl etherate and aluminum-sec-butoxide were used as the catalysts of epoxide polymerization. Aluminum butoxyethoxide was prepared from aluminum-sec-butoxide and 2-butoxyethanol according to the procedure described in Ref. [21]. It was reported that there were little differences in catalytic effects between aluminum butoxyethoxide and aluminum-sec-butoxide [22]. However, because of easy handling of aluminum butoxyethoxide, it was selected as precursor. 1 mole GPTS was prehydrolyzed with 1.5 mole water in the presence of 0.1 M HCl and TMOS was added to the prehydrolyzed GPTS solution at molar ratio GPTS:TMOS = 7:3 and 6:4. Additional amounts of water ( $H_2O:OR = 2:1$ ) and ethanol for dilution were added and stirred for 12 hours at room temperature. This buffer sol was used as a base solution, which will be called the GM in this study. Final sols were prepared by adding the different amounts of aluminum butoxyethoxide to GM, with molar ratios with respect to Si of 0.03 (GMA3), 0.05 (GMA5), 0.1 (GMA10), 0.2 (GMA20) and 0.3 (GMA30). After the addition of aluminum butoxyethoxide, the sols were left with stirring 2 hours at 0–5°C.

In order to compare the catalytic effects of aluminum butoxyethoxide, another catalyst of boron trifluoride diethyl etherate, was added to GM with molar ratios

with respect to Si of 0.03 (GMB3), 0.05 (GMB5) and 0.1 (GMB10).

### 2.2. Preparation of Coatings

10 × 10 cm PMMA substrates with thickness of 2 mm were cleaned with isopropanol before use and silicon wafer were used as substrate for fourier transformation infrared spectroscopy (FT-IR) measurement. The coatings were carried out on the substrates in dipping-withdrawing manner, in a humidity-controlled box, with a relative humidity below 40%, at the room temperature. In order to obtain uniform thickness in all the samples, the withdrawing speed was controlled. The coatings were dried at 120°C for 2 hours.

### 2.3. Measurements

The coating thickness was measured with a profilometer (Alpha Step 200. Tencer Instrument) on the step made by scratching the coating after the deposition of single layer.

The  $^{29}Si$  and  $^{13}C$  NMR spectra were obtained using a Bruker AC 300 spectrometer (liquid-state). All NMR measurements were performed in  $CDCl_3$ , used as received, by preparing the samples in 1:1 solvent/reaction mixture solution. The  $^{13}C$  chemical shifts were measured to external tetramethylsilane(TMS) and phenyltrimethylsilane was used as internal standard for quantitative evaluation of epoxide ring and its derivatives. The  $^{29}Si$  chemical shifts were measured relative to tetramethylsilane. Two milligrams of chromium (III) acetylacetonate as relaxation agent was added to the samples for the  $^{29}Si$  NMR determination. The quantitative evaluation of the liquid state NMR spectra, which were recorded at identical acquisition parameters, was performed by comparison of the integrated signal intensity with that of the internal phenyltrimethylsilane standard.

Infrared absorption spectra in the range 4000–400  $cm^{-1}$  were recorded by fourier transformation infrared spectroscopy (FT-IR) (Bruker EQUINOX55) with a resolution 4  $cm^{-1}$  on films coated on silicon substrate. The hardness of the coatings on PMMA substrates was determined by a nanoindenter (Nano Instruments.) The continuous stiffness measurement was used and the maximum load was 20 mN. The hardness was calculated from the indentation load-displacement data [23].

### 3. Results

#### 3.1. NMR Spectra

In order to investigate the organic polymerization and inorganic condensation by catalytic effect of aluminum butoxyethoxide, the <sup>13</sup>C NMR spectra of the solutions with different amount of aluminum butoxyethoxide (with molar ratios with respect to Si of 0, 0.03, 0.05, 0.1, 0.3) were measured. Figure 1 shows the <sup>13</sup>C NMR spectra of GM and the assignment of the signals can be shown in Table 1 [13, 24–26]. The <sup>13</sup>C NMR spectrum of the GM (Fig. 1(a)) clearly indicated the occurrence of the hydrolysis reaction without cleavage of the epoxide rings, as shown by the maintenance of the doublet signals at peaks 5 and 6. This result agrees with those in previous reports [13, 16]. However, after addition of aluminum butoxyethoxide as a catalyst, two peaks of the epoxide ring decrease and several new peaks

(g, h, i, k, P) are present in the Fig. 1(b) and (c), clearly indicating that aluminum butoxyethoxide induces the epoxide ring-opening reaction. These peaks are produced by additional reactions of opened epoxide ring with methanol and water. Alkylether (h, i) and diol (k) are formed by reaction of alcohol and water with the epoxide ring. Poly (ethylene oxide) chains (P) are produced by polymerization reaction between epoxide rings.

In Fig. 1, although higher amount of aluminum butoxyethoxide induced more opened epoxide-ring, the signal intensities of poly(ethylene oxide) chains around 74 ppm was remained without significant changes. Thus, poly(ethylene oxide) chains is saturated above 10 mol% of aluminum butoxyethoxide.

Figure 2 shows the amount of epoxide existed in the sol as a function of aluminum butoxyethoxide concentration. The amount of epoxide can be calculated from relative intensity of the epoxide ring peaks in NMR

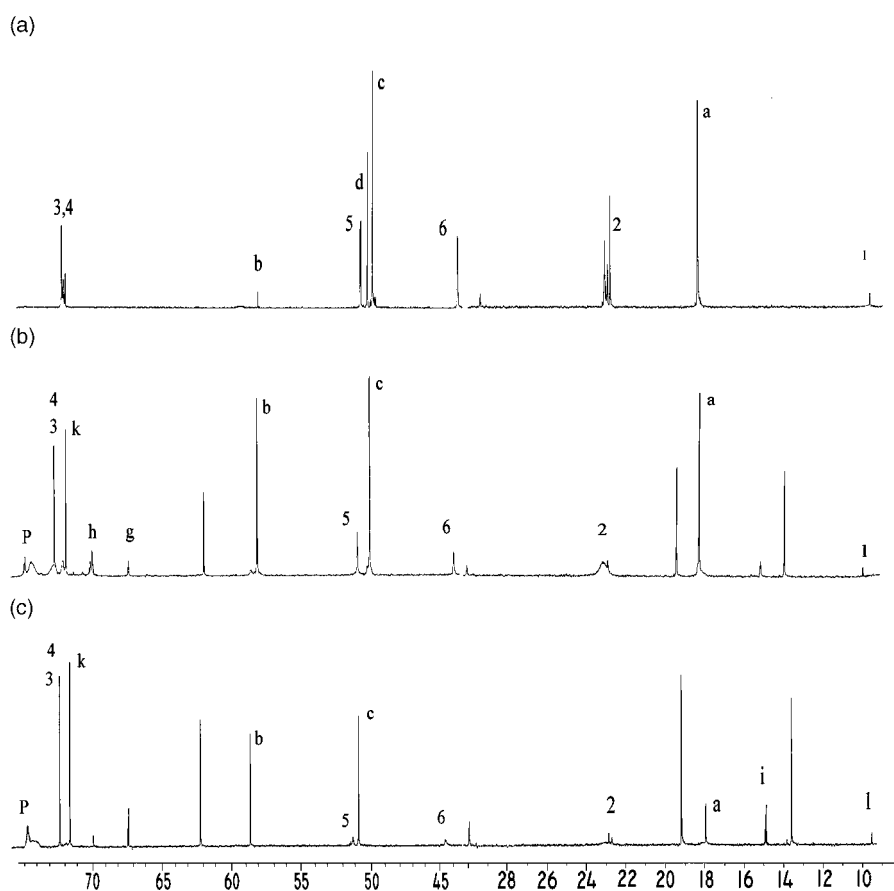
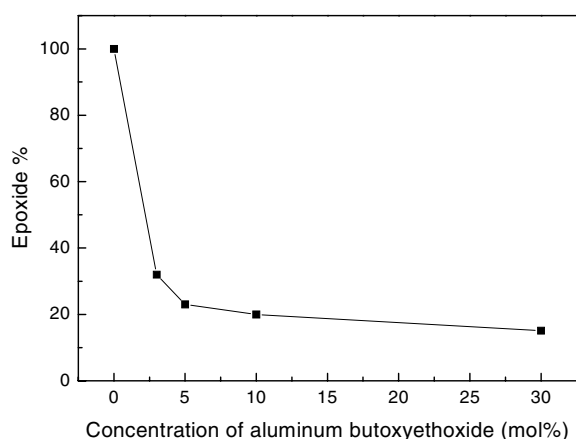


Figure 1. <sup>13</sup>C NMR spectra of (a) GM, (b) GMA10, and (c) GM30 sols in the range 0–80 ppm.

Table 1. The assignment of signals in  $^{13}\text{C}$  NMR spectra of GMA0, GMA10 and GMA30 sols.

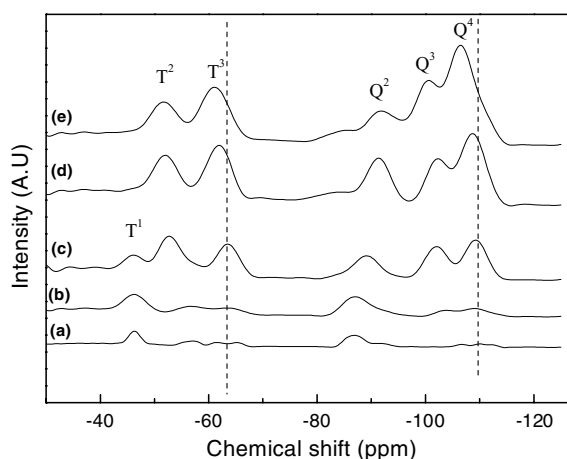
Abbreviation	$^{13}\text{C}$ chemical shift (in ppm)	Structural group
1	4.84	$\text{CH}_2\text{CHOCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{-Si-}$
2	22.45	$\text{CH}_2\text{CHOCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{-Si-}$
3	73.05	$\text{CH}_2\text{CHOCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{-Si-}$
4	71.03	$\text{CH}_2\text{CHOCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{-Si-}$
5	50.38	$\text{CH}_2\text{CHOCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{-Si-}$
6	43.69	$\text{CH}_2\text{CHOCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{-Si-}$
a	18.1	$\text{CH}_3\text{-CH}_2\text{-OH}$
b	57.7	$\text{CH}_3\text{-CH}_2\text{-OH}$
c	49.5	$\text{CH}_3\text{OH}$
d	50.4	$\text{CH}_3\text{-O-Si}$
e	18.5	$\text{CH}_3\text{-CH}_2\text{-O-Si}$
f	58.4	$\text{CH}_3\text{-CH}_2\text{-O-Si}$
g	64.1	$\text{CH}_2(\text{OH})\text{-CH}(\text{OH})\text{-CH}_2\text{-}$
h	67.1	$\text{CH}_2(\text{OCH}_2\text{-CH}_3)\text{-CH}(\text{OH})\text{-CH}_2\text{-}$
i	15.3	$\text{CH}_2(\text{OCH}_2\text{-CH}_3)\text{-CH}(\text{OH})\text{-CH}_2\text{-}$
k	71.3	$\text{CH}_2(\text{OH})\text{-CH}(\text{OH})\text{-CH}_2\text{-}$
P	Above 74	Poly(ethylenoxide)

spectra of each solution, assuming that there was no opened epoxide ring in aluminum-free sol. This represents that aluminum butoxyethoxide is a very strong catalyst for epoxide ring opening and the epoxide ring opening is almost made with the small addition of aluminum butoxyethoxide. Thus, the amount of 10 mol% aluminum butoxyethoxide has the most effective activity for epoxide ring opening reaction. This reactivity of the aluminum butoxyethoxide in the sols is in agree-

Figure 2. The amount of epoxide in GMA sols evaluated from  $^{13}\text{C}$  NMR spectra.

ment with that reported [22]. It was reported the long preparation time of the sols before addition of catalyst is expected to induce the gradual increase of the ring-opening rate and about 24 hours are needed for complete opening of epoxide [22]. Our result shows the 10 mol% of aluminum butoxyethoxide leads to 80% ring-opening after 3 hours for reaction time.

The  $^{29}\text{Si}$  NMR measurements were also determined (Fig. 3). The  $^{29}\text{Si}$  NMR spectrum of the Al-containing

Figure 3.  $^{29}\text{Si}$  NMR spectra of (a) GM, (b) GMA3, (c) GMA5, (d) GMA10, and (e) GMA30.

sols shows the formation of one ( $T^1$ ,  $Q^1$ ), two ( $T^2$ ,  $Q^2$ ), three ( $T^3$ ,  $Q^3$ ) and four ( $Q^4$ ) new siloxane bonds from GPTS and TMOS. As concentration of aluminum butoxyethoxide increases, the intensity of the peaks with  $T^3$ ,  $Q^3$  and  $Q^4$  increases, which is indication of higher degree of condensation. The addition of aluminum butoxyethoxide to the sols leads to another changes in the spectra. The peaks become broader and the maxima of  $T^3$ ,  $Q^3$ ,  $Q^4$  groups are shifted to lower field about 3–8 ppm, respectively. The existence of Si–O–Al bonding is supported by the low field shift of the peak maxima, because it is known that the chemical shift of silicon atoms with aluminum in their second coordination sphere (Si–O–Al) is moved in this direction [27]. The extent of low field chemical shift of peak maxima is proportional to the number of Si–O–Al bonds. In the  $^{29}\text{Si}$  NMR spectra, it can be seen that the sol of 30 mol% of aluminum butoxyethoxide has highest chemical shift and greatest amounts of Si–O–Al bonds. Figure 4 shows the degree of condensation of the sols, calculated from Fig. 3, with aluminum butoxyethoxide contents. The calculation of the degree of condensation was made by [17]. The degree of condensation calculated from NMR spectra is saturated as concentration of aluminum butoxyethoxide increases.

Highly condensed sols can be obtained by addition of aluminum butoxyethoxide to sols at room temperature. Also, it can be seen that aluminum butoxyethoxide has a strong catalytic effect on the condensation reaction.

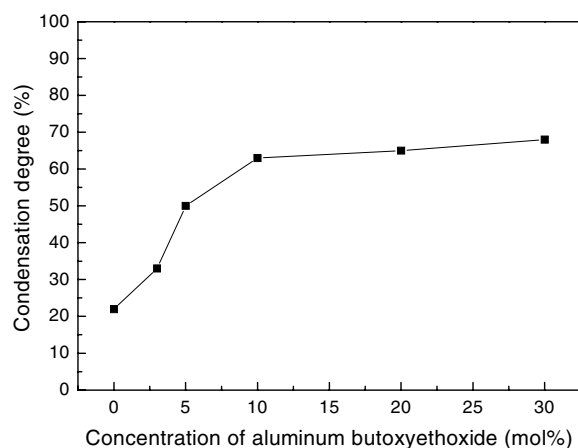


Figure 4. The degree of condensation in GMA sols as a function of concentration of aluminum butoxyethoxide.

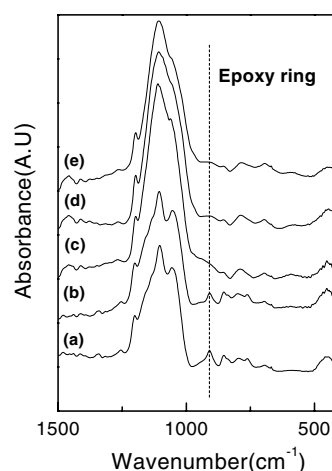


Figure 5. FT-IR spectra of (a) GM coating dried at  $120^\circ\text{C}$  for 0 hours, (b) GM coating dried at  $120^\circ\text{C}$  for 2 hours, (c) GMA10 coating dried at  $120^\circ\text{C}$  for 2 hours, (d) GMA20 coating dried at  $120^\circ\text{C}$  for 2 hours and (e) GMA30 coating dried at  $120^\circ\text{C}$  for 2 hours.

### 3.2. FT-IR Spectra

The epoxides have characteristic IR absorption bands at  $950\text{--}810$  (asymmetrical ring stretching)  $\text{cm}^{-1}$ . In our work,  $910\text{ cm}^{-1}$  was used as a reference for the evaluation of the epoxide polymerization in the solid state. The characteristic bands of epoxides are still clearly detectable in GM deposited coatings (Fig. 5). The FT-IR spectra of the coatings, which contain an increasing amount of aluminum butoxyethoxide, shows a decrease in the intensity of epoxide band with increase of aluminum butoxyethoxide in sols. The reduction in intensity of the epoxide band with higher aluminum butoxyethoxide contents and heat treatment is attributed to the epoxide ring opening catalyzed by aluminum butoxyethoxide. Also, Fig. 5 shows the catalytic effect is stronger than thermal effect. In absence of aluminum butoxyethoxide, there was a slightly smaller decrease of epoxide.

FT-IR spectra in Fig. 5 shows that the coated films have a strong absorption band around  $1100\text{ cm}^{-1}$ , attributed to asymmetric stretching of Si–O–Si bonds [28, 29]. This peak was found to shift to higher frequencies with the thermal treatment and to change the position as a function of the catalyst used in the sol-gel reaction. The exact positions of the  $1100\text{ cm}^{-1}$  band in the different samples are indicated in Fig. 6. In all the samples, a shift to higher frequencies after thermal curing and with higher contents of catalyst is observed. The shift of the stretching vibration of Si–O–Si to

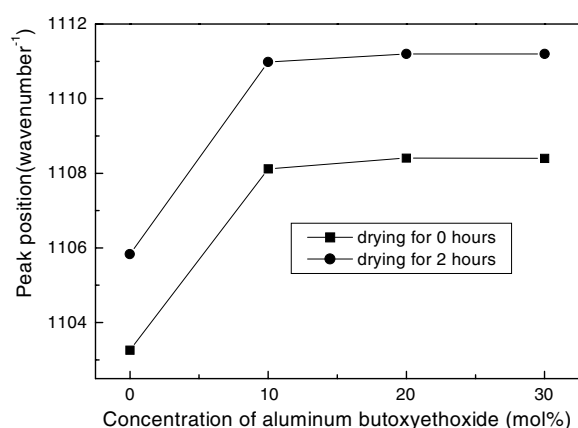


Figure 6. Peak position of Si—O—Si band in FT-IR spectra as a function of concentration of aluminum butoxyethoxide.

higher frequencies is correlated to a strengthening of the network [30].

### 3.3. Hardness

The continuous stiffness measurement provides a method of measuring continuously the film stiffness without the need for discrete unloading cycles, which allows measurements to be made at small penetration displacement for ultra thin film [23]. The thickness of the coating used nanoindentation measurement is above 1  $\mu\text{m}$ , which is thick enough for evaluation of the film hardness without influence from substrate. The hardness of PMMA and soda-lime glass substrate measured by nanoindenter was about 180 and 310 Mpa. Figure 7 shows the hardness of the coatings as a function of aluminum butoxyethoxide contents. When the GPTS content is higher, the coating has higher hardness. This means the increase of hardness by inorganic condensation is larger than that by epoxide polymerization.

When the amount of aluminum butoxyethoxide increases to 10 mol%, the hardness of the coating increases suddenly. When the aluminum content is more than 10 mol%, it can be seen that the hardness of the coating increases almost linearly with aluminum content. Boron trifluoride diethyl etherate was added instead of aluminum butoxyethoxide in order to compare the increase of hardness by aluminum butoxyethoxide with by different catalyst. It was reported boron trifluoride has the similar catalytic effects like aluminum butoxyethoxide [16]. In case of coatings obtained from GMB3, GMB5 and GMB10, the hardness of all the

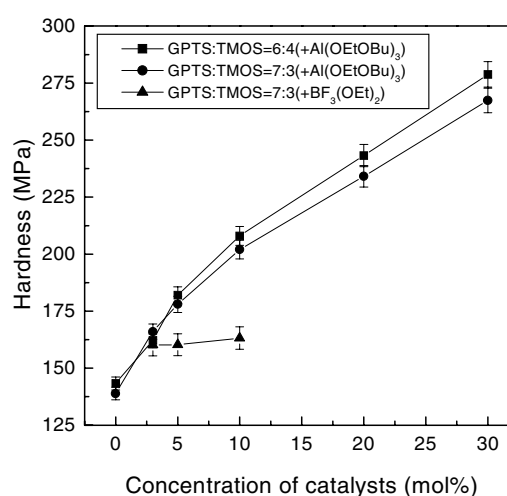


Figure 7. Hardness of the coatings as a function of concentration of aluminum butoxyethoxide or boron trifluoride diethyl etherate.

samples have the similar values. The cause of this result was that the catalytic effect of aluminum butoxyethoxide on condensation reaction is larger than that of boron trifluoride diethyl etherate.

## 4. Discussion

In sol-gel process of the GPTS based materials, catalysts are necessary for the hydrolysis and condensation reactions together with a strong catalytic effects of epoxide polymerization. The NMR and FT-IR data definitely reveal the catalytic effects of aluminum butoxyethoxide on the epoxide ring opening reaction and condensation reaction. At 10 mol% of aluminum butoxyethoxide, the catalytic effects of aluminum butoxyethoxide was saturated. This result may be because the reactivity of the aluminum butoxyethoxide about reactions was related with the size of Al species which were produced by hydrolysis and condensation of aluminum butoxyethoxide. Aluminum butoxyethoxide is converted to low-molecular hydrolysis and condensation products in the presence of low water content. Low molecular condensed species of aluminum butoxyethoxide has easier accessibility to reaction sites for catalytic reaction. Thus, high molecular condensed species formed in higher concentration of aluminum butoxyethoxide has lower activity respectively. The similar results were previously reported in the GPTS-Ti-alkoxide systems [22]. In case of Ti alkoxide, which possesses the similar catalytic reactivity, high concentration of Ti-alkoxide leads to lower degree of

condensation compared with that of low concentration. Figures 2 and 4 show that aluminum butoxyethoxide has the most effective activity in case of 10 mol% concentration meaning the surface of Al species may have the most efficient distribution. Therefore, higher concentration of aluminum butoxyethoxide may induce the decrease of the catalytic effect in the sols.

In Fig. 7, hardness of the coatings increases above 10 mol%, although the catalytic effects of aluminum butoxyethoxide is saturated at 10 mol%. The additional increase of hardness above 10 mol% may be explained by another effect of catalyst. Aluminum butoxyethoxide become parts of the inorganic network when higher concentration of catalysts was involved. This behavior can be explained by formation of Si—O—Al. In <sup>29</sup>Si NMR data, the low field chemical shifts of peak maxima due to Si—O—Al bonds were happened when the concentration of aluminum butoxyethoxide was larger than 10 mol%. Thus, the Si—O—Al can be formed because aluminum butoxyethoxides took parts in structural elements of inorganic network.

Different hardening mechanism of the coatings may be suggested as a function of the amount of aluminum concentration. Below Al 10 mol%, the hardness was dominated by epoxide polymerization and condensation. Thus, there was abrupt increase in hardness of coating by mainly catalytic effects of aluminum butoxyethoxide. Above 10 mol%, the degree of epoxide polymerization and condensation was saturated and some of aluminum butoxyethoxide used as catalyst took parts in structural elements of inorganic network. Thus, the increase of hardness has a linear relationship with concentration of aluminum butoxyethoxide, because the formation of oxide networks, which were generated from catalysts, is linearly proportional to the contents of aluminum butoxyethoxide.

## 5. Conclusion

The addition of aluminum butoxyethoxide in the sol of GPTS and TMOS catalyzed the epoxide ring opening and the condensation reaction increasing the cross-linking degree of inorganic network. The opened epoxide converted to alkyether, diol, poly(ethylene oxide). Below 10 Al mol%, hardness of the coatings was mainly determined by epoxide polymerization and condensation reaction, governed the mainly catalytic effects. Above 10 Al mol%, the hardness of coatings

was mainly determined by formation of oxide network (Si—O—Al).

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